California Environmental Protection Agency

Air Resources Board

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PROCEDURE FOR THE ANALYSIS OF POLYNUCLEAR AROMATIC HYDROCARBONS AND TOTAL AROMATIC HYDROCARBONS IN DIESEL FUELS BY SUPERCRITICAL FLUID CHROMATOGRAPHY AND FLAME IONIZATION DETECTOR

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1 **Introduction**

- 1.1 This document describes an automated method for the determination of total aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAH) in diesel fuel.
- 1.2 The range of aromatics concentrations to which this test method is applicable is from 1 to 75 mass %. The range of PAH concentrations to which this test method is applicable is from 0.5 to 50 mass %.
- 1.3 This procedure is based on ASTM D5186-96¹.

2. **Method**

- 2.1 The diesel sample is injected onto a packed silica adsorption column and the saturated, monocyclic aromatic and PAH fractions are eluted using supercritical carbon dioxide as the mobile phase.
- 2.2 A flame ionization detector (FID) is used to detect these three groups.
- 2.3 The chromatographic areas corresponding to the nonaromatic, monocyclic aromatic, and PAH fractions are determined and the mass percent content of each group in the fuel is calculated by normalization.

3 **Instrument**

- 3.1 Hewlett-Packard model G1205A Supercritical Fluid Chromatograph (SFC)
- 3.1.1 Hewlett-Packard model 7673 autosampler
- 3.1.2 Hewlett-Packard SFC Chemstation software
- 3.1.3 HP 5890 series II chromatograph
- 3.1.4 50 microliter single taper syringe
- 3.1.5 0.5 microliter internal loop.
- 3.1.6 HP Hydrocarbon Group Separation Column, 250 mm long x 4.6 mm ID, 5 micron, 10 angstrom or equivalent
- 3.2 Computer system running Windows 3.1 or Windows 95

- 3.3 Flame ionization detector
- 3.4 Restrictor: see 5.1 below

4. Reagents

- 4.1 Purity of reagents: Unless otherwise specified, any chemicals used shall be American Chemical Society (ACS) reagent grade or better.
- 4.2 Carbon dioxide (CO₂), chromatographic grade, 99.995% minimum purity, supplied in a pressurized cylinder equipped with a dip tube for the removal of liquid CO₂.
- 4.3 Naphthalene, 99+%
- 4.4 1,2,3,4-tetrahydronaphthalene (tetralin), 99% purity
- 4.5 Toluene, 99.8%, HPLC grade
- 4.6 Hexadecane, 99+%, anhydrous
- 4.7 Air, ultra zero grade (hydrocarbon free), supplied by Air Products
- 4.8 Hydrogen, 99.99% purity
- 4.9 Nitrogen
- 4.10 Helium, commercial grade

5. **Preparation of Instrument**

5.1 The HP SFC is configured as follows:

FID gases:

hydrogen at approximately 30 mL/min air at approximately 400 mL/min

FID temperature: 275 °C

Column temperature: 34 °C (isothermal) Injector temperature: room temperature

Auxiliary zone temperature: 100⁰ Pressure: isobaric at 140 bars

Flow: 2.4 mL/min

Number of solvent washes: 12

Number of sample washes: 10

Run time: 14 minutes for diesel samples and 6 minutes for the performance mixture.

Restrictor: low flow restrictor. One end of the restrictor is inserted into the tip of the FID and this restrictor is lowered or raised inside the FID until the correct relative response factors of toluene, tetralin and naphthalene (relative to hexadecane) are obtained (see section 10.4 below). The other end of the restrictor is connected to the outlet end of the column.

Note: The column temperature and pressure may be adjusted as the column deteriorates.

6. **Calibration**

- 6.1 This method is based on normalization. No calibration is required.
- 6.2 Detector accuracy, resolution, and retention time repeatability are regularly checked (see section 10 below) with a performance mixture made up of the following components, all weighed to the nearest 0.01 g:

2 g naphthalene20 g toluene3 g tetralin75 g hexadecane

The naphthalene may take several hours to dissolve completely.

7. **Procedure**

- 7.1 2 mL of each sample is transferred into a glass autosampler vial and capped.
- 7.2 $25 \mu L$ is injected into the instrument by the autosampler.
- 7.3 The chromatographic response is integrated by the data system. Results are calculated as described in section 9.

8. **Safety**

- 8.1 Diesel fuel and many of its various components are toxic and flammable. Persons using this method must wear protective gloves and eyewear when working with reagents and samples. Reagents and samples are used in a fume hood with adequate ventilation.
- 8.2 All compressed gas cylinders present hazards and should be handled appropriately. Hydrogen is extremely flammable.

9. **Calculations**

- 9.1 The chromatogram is divided into three sections, each integrated as a single component.
- 9.1.1 The first section runs from sample injection to the bottom of the lowest valley between the retention times of hexadecane and toluene (determined from the performance mixture analysis, see section10.5 below.) This area represents the nonaromatic fraction of the sample.
- 9.1.2 The second section runs from the end of the first section to the beginning of the performance mixture's naphthalene peak (see section 10.5 below). This area represents the monocyclic aromatic fraction of the sample.
- 9.1.3 The third section runs from the end of the second section until the end of the chromatogram. The operator may choose to end the third section earlier to avoid errors due to slight drifts in the baseline. This area represents the PAH fraction of the sample.
- 9.2 The mass % of each fuel fraction is equal to the area percent of its corresponding chromatographic section. The total aromatic concentration is the sum of the monocyclic and polycyclic aromatic concentrations.
- 9.3 In some regulatory cases, total aromatic concentration in volume % is required. ARB and the Western States Petroleum Association (WSPA) have agreed on a correlation equation between mass and volume %. The equation used is:

Total aromatics (volume %) = 0.916 x total aromatics (mass %) +1.33

10 **Quality Control**

10.1 The performance mixture described in section 6.2 above is analyzed twice at the beginning of the analysis day, once after every five samples, and once again at the end of the analysis day. The analyses serve four functions:

10.1.1 Detector resolution is checked with every performance mixture analysis according to the following equations:

$$R_{NM} = \frac{2*(t_2-t_1)}{1.699*(y_2+y_1)}$$

$$R_{MP} = \frac{2*(t_4-t_3)}{1.699*(y_4+y_3)}$$

Where: R_{NM} = resolution between the nonaromatic and monoaromatic peaks

 R_{MP} = resolution between the monoaromatic and polycyclic aromatic peaks

 $t_1 = time$ (seconds) for the n-C₁₆ peak apex

 t_2 = time (seconds) for the toluene peak apex

 t_3 = time (seconds) for the tetralin peak apex

 t_4 = time (seconds) for the naphthalene peak apex

 y_1 = peak width at half height (seconds) of the hexadecane peak

 y_2 = peak width at half height (seconds) of the toluene peak

 y_3 = peak width at half height (seconds) of the tetralin peak

 y_4 = peak width at half height (seconds) of the naphthalene peak

 R_{NM} must be at least four and R_{MP} must be at least two in order for the detector to pass the resolution test. A macro (psintres.mac) designed for Microsoft Excel is normally used to calculate these quantities.

- 10.1.2 Retention time repeatability is checked using the initial two performance mixture analyses of the day. The retention times of hexadecane and toluene must not differ by more than 0.5% between the two runs.
- 10.1.3 Detector accuracy is checked with every performance mixture analysis. For each component of the performance mixture, a relative response factor is determined from the chromatogram according to the following equations:

$$RF_i \ = \frac{A_i}{M_i}$$

$$RRF_{i} = \underbrace{\begin{array}{c} RF_{i} \\ RF_{C10} \end{array}}$$

where

A_{i}	=	Area % of component I in the performance mixture
$M_{\rm i}$	=	Known mass % of component I in the performance mixture
RF_{i}	=	Response Factor of component I
RF_{C16}	₅ =	Response Factor of hexadecane in the performance mixture
RRF_i	=	Relative Response Factor of component I

These empirical relative response factors are compared with theoretical relative response factors calculated by the following equations:

$$RRF_{theor} = \frac{(12.01n)}{MW} \times \frac{(226.4)}{12.01 \times 16}$$

where:

12.01 = the atomic mass of carbon

n = the number of carbon atoms in the component molecule

MW = molecular mass of the component molecule

226.4 = molecular mass of hexadecane

16 = the number of carbon atoms in hexadecane

The measured RRF_i for each component (toluene, tetralin and naphthalene) in the test mixture must be within 10% of the theoretical value as calculated with the above equation or summarized in Table 1. The macro psintres.mac will automatically perform these calculations.

- 10.1.4 The beginning time of the naphthalene peak is determined for every performance mixture analysis. This time is used in calculating results for the next set of samples (see sections 9.1.1 through 9.1.3 above.)
- 10.2 If any of the tests in section 10.1 above result in a failure, appropriate corrective action must be taken and the performance mixture rerun before any more samples may be analyzed.
- 10.3 Pure hexadecane is run as a blank once during each analysis day. If the total aromatics result is greater than 0.5 mass % or the PAH result is greater than 0.2 mass %, corrective action must be taken.
- 10.4 One or more control samples must be run each analysis day.

- 10.4.1 Each sample to be analyzed must fall within 5 mass % total aromatics and 1.5 mass % PAH of at least one of the control samples.
- 10.4.2 Each control sample analysis must be within the published reproducibility (see section 10.4.4 below) of either:
 - a. The accepted values determined from interlaboratory testing or
 - b. The running average values determined on the instrument being used if no interlaboratory testing data is available.
- 10.4.3 If any control sample falls outside the acceptable range, corrective action must be taken and the sample reanalyzed before any analyte samples can be run.
- 10.4.4 The reproducibilities for total aromatics and PAH are given by the following equations:

Total aromatics: R = 0.75 (aromatics mass%)^{0.23}

PAH: $R = 0.47 \text{ (PAH mass\%)}^{0.45}$

10.4.5 Some potential control samples with consensus values are as follows:

Sample	Total Aromatics	PAH
DL9802	22.7	4.1
DL9806	32.5	4.2
WSPA	14.5	2.4

- 10.5 At least one analyte sample must be run in duplicate. The duplicate results must not differ by more than the ASTM reproducibility, which is defined as:
 - 0.16(total aromatics)^{0.23} and
 - 0.16(PAH)^{0.16} for PAH less than 5 mass %, or
 - $0.36 (PAH)^{0.13}~$ for PAH greater than 10 mass $\%\,.$

Note that repeatability is not currently defined for samples between 5 and 10 mass % PAH. Samples in this range should not be used for meeting the duplicate analysis requirement.

- 10.6 Once per year, the detector linearity is checked.
- 10.6.1 Accurately weighed blends (1:1 and 3:1 dilutions) of a motor diesel fuel in hexadecane are prepared.
- 10.6.2 The original fuel and the dilutions are analyzed as normal samples.
- 10.6.3 Using the results obtained for the different dilutions, calculate the expected concentration of aromatic hydrocarbons in the original diesel fuel using the following equation:

$$B = A * D / (C + D)$$

Where:

A = mass % aromatic hydrocarbons in the original fuel

B = mass % aromatic hydrocarbons in the diluted fuel

C = mass of hexadecane in the dilution

D = mass of original diesel fuel in the dilution

- 10.6.4 Compare the results obtained for mass percent aromatics in the original diesel fuel with the results obtained from the two dilutions. These values should agree to within the repeatability limits as stated in section 10.9. If agreement is not obtained, corrective action must be taken.
- 10.7 Once per year, the limit of detection is determined. A diesel sample is serially diluted with hexadecane to five different concentrations. Each dilution is analyzed as a normal sample, with the lowest concentration repeated several times. The limit of detection is calculated using the following equation:

$$LOD = (|b| + t*s)/m$$

where: b = intercept

t = t-value for n analyses

s = standard deviation at lowest concentration

m = slope

n = number of replicates

11 References

11.1 "Standard Test Method for Determination of the Aromatic Content of Diesel Fuels and Aviation Turbine Fuels by Supercritical Fluid Chromatography," *Annual Book of ASTM Standards*, Vol 05.03.

TABLE 1: Theoretical Response Factors

Component	Carbons	Molecular Mass	RRF(Theor)
Toluene	7	92.13	1.075
Tetralin	10	132.2	1.070
Naphthalene	10	128.2	1.104